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Published in:
Applied Physics Letters

DOI:
10.1063/1.3508948

Crossbar memory array of organic bistable rectifying diodes for nonvolatile data storage

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(Received 13 September 2010; accepted 10 October 2010; published online 11 November 2010)

Cross-talk in memories using resistive switches in a cross-bar geometry can be prevented by integration of a rectifying diode. We present a functional cross bar memory array using a phase separated blend of a ferroelectric and a semiconducting polymer as storage medium. Each intersection acts simultaneously as a bistable rectifying diode. A logic table of a 4-bit memory and integration into a 3×3 cross bar array are demonstrated. The most difficult state, a high resistance bit completely surrounded by low resistance bits could be unambiguously identified. © *2010 American Institute of Physics*. [doi:10.1063/1.3508948]

Essential for most envisioned applications of organic electronics is nonvolatile data storage.[1] Preferably the memory should retain its data when the power is turned off. Furthermore the memory should be programmed, erased, and read-out electrically.[2] The ultimate memory relies on resistance switching where the discrete elements are integrated in a cross-bar array,[3,4] i.e., an unpatterned storage medium that is sandwiched between rows and columns of metal electrode lines where each intersection makes up one memory bit.

However, technologies based on resistive switches are prone to cross-talk.[5] As an illustration we consider a 4-bit array of bistable resistors, schematically presented in Fig. 1(a). We would like to address the high resistive off-state of the bit W1B1 formed by word-line W1 and bit-line B1. The three neighboring bits are in the low resistive on-state. Addressing of the high resistance W1B1 bit by applying a voltage difference between W1 and B1 is hampered by the low resistance parasitic path along the three neighboring bits. Consequently, the logic state of the W1B1 bit cannot reliably be read-out. To circumvent the cross-talk without patterning the storage medium, a rectifying diode must be added in series with each discrete switch, as shown in Fig. 1(b). The parasitic leakage path is then disabled by the reverse biased diode of the W2B2 bit. By applying a bias on appropriate rows and columns, the logic states, "0" or "1," of each individual bit can now unambiguously be addressed. Such a cross-bar memory with an unpatterned storage medium and the size of a single bit equal to $4F^2$, F being the electrode linewidth and spacing, is termed the "immortal memory."[3]

Discrete resistive switches have been realized using phase separated blends of a ferroelectric polymer with a semiconducting polymer. Spin-coated films consist of semiconducting domains, continuous from top to bottom, embedded in a ferroelectric matrix.[6,7] The microstructure of the blend used in our study, probed with scanning electron microscopy (SEM) is shown in Fig. 2(a). The blend phase separated into semiconductor-rich (spheres) and ferroelectric-rich (star-shaped matrix) domains. Schematic presentation of a diode based on the blend is given as an inset in Fig. 2(b). The polarization field of the ferroelectric modulates the injection barrier at the semiconductor contact. The diodes can be switched at biases larger than the coercive field. The resistance can be read-out nondestructively at low bias. Both symmetric and rectifying diodes have been reported with current modulation up to six orders of magnitude. Here we demonstrate integration of discrete diodes into functional cross-bar memory arrays. We present the method by which, each individual bits in the array are programmed and read out nondestructively.

As ferroelectric polymer we used the random copolymer [poly(vinylidene fluoride-cotrifluoroethylene)] [P(VDF-TrFE)] (80%–20%) (Solvay, Belgium), and as semiconductor poly(9,9-dioctylfluorenyl-2,7-diyl) end-capped with dimethylphenyl groups (PFO) (American Dye Source). Both materials were utilized as received. P(VDF-TrFE) was dissolved in distilled tetrahydrofuran (THF), with a concentration of 50 mg/ml. Blend solutions of 30 mg/ml were prepared by co-dissolving P(VDF-TrFE) and PFO in distilled THF and filtered over 1 μm PTFE filters. The mixing ratio of the two polymers PFO:P(VDF-TrFE) was kept at 10:90 in weight. Memory arrays were fabricated on cleaned glass substrates. Au bottom electrodes (15 nm) with a 1 nm Cr adhesion layer were evaporated via a shadow mask. Blend thin films of

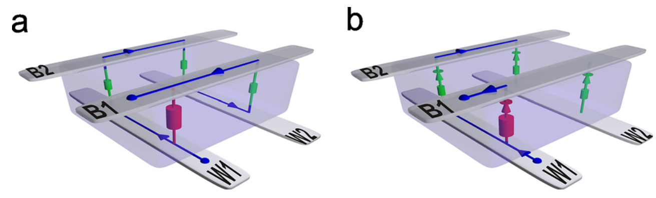

FIG. 1. (Color online) Schematic presentation of the origin of cross-talk in 4-bit memory array. The cross bars consist of two word lines (W) and two bit lines (B). W1B1 is set to "0" while the other three bits are set to "1." (a) An array based on resistive switches. (b) An array of resistive switches with integrated rectifying diodes.

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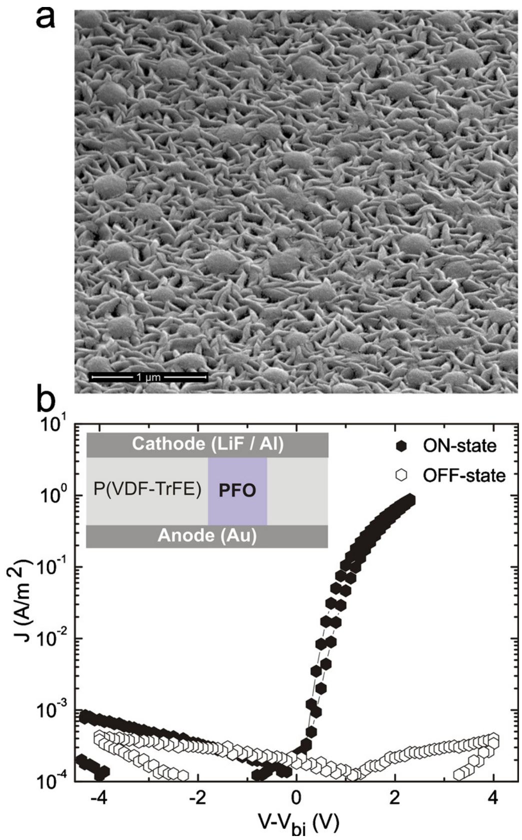

FIG. 2. (Color online) (a) SEM micrograph of the phase separated morphology and (b) J-V characteristics of a bistable rectifying diode based on a phase separated 10/90 wt % blend of a ferroelectric polymer, P(VDF-TrFE) and a semiconducting polymer, PFO. SEM was taken at a tilt angel of 52°. The diode is fabricated with a gold bottom electrode and a LiF/Al top electrode. Device area amounted to 1 mm^2. The diode is poled with pulses of +/−20 V, exceeding the coercive field. The voltage axis is corrected for the built-in voltage of about 1.5 V. The inset in part (b) shows the device layout.

300–400 nm were spin coated and annealed for 2 h at 140 °C in vacuum to enhance the crystallinity of the P(VDF-TrFE) phase.[8] LiF (1 nm) capped with 70 nm Al was used as top electrode. The dimension of the active area of one bit was either 1×1 mm^2 or 3×3 mm^2. All the device preparation steps were conducted in nitrogen filled glove boxes. SEM was used to probe the morphology of the blend. The normal mode (detection of secondary electrons) with acceleration voltage of 2.0 kV was used. Ferroelectric characterizations of the capacitor and discrete diode were done by Sawyer–Tower technique or pulse technique.[9] The ferroelectric polarization and coercive field of neat P(VDF-TrFE) capacitors amounted to 0.06 C/m^2 and 50 MV/m, respectively, in good agreement with literature data.[8,9] The remnant polarization of the blends, measured with a pulse technique, amounted to about 90% of that of neat P(VDF-TrFE) capacitors, i.e., ~0.05 C/m^2. All the current-voltage measurements were conducted in vacuum, 1×10^{-6} mbar with a Keithley 4200 semiconductor characterization system. Bias was appropriately applied on both bottom and the top electrodes.

The current density as a function of bias of a discrete blend diode is presented in Fig. 2(b). The diode is poled at either +/−20 V exceeding the coercive field. Both LiF and Au form an injection limited contact on PFO.[10,11] The barrier for electron and hole injection is 0.8 eV and 1.3 eV, respectively. In the off-state the ferroelectric polarization points toward the cathode. Effectively, both injection barriers then increase and no current is flowing irrespective of the bias.[12] In the on-state the ferroelectric polarization points toward the anode and both injection barriers effectively can be disregarded.[12] In the forward direction holes are injected from gold and electrons from LiF/Al. In the reverse direction there is no current flowing, holes and cannot be injected form LiF/Al and electrons cannot be injected form gold. The final result is a bistable rectifying diode.

The smallest array comprises two word lines and two bit lines, yielding 4 bits with 16 different logic states. First, all pixels are put in the off-state. To program each individual bit, a programming voltage pulse exceeding the coercive field of P(VDF-TrFE) is required, i.e., +/−20 V. In order to prevent any effect of the programming pulse on the logic state of the neighboring bits, we applied half the programming voltage (+/−10 V) on the word line and half of the voltage (−/+10 V) on the bit-line. All other lines were grounded. In this way the neighboring bits experience a field below the coercive field and their logic state remains unaffected. After programming the logic state of each individual bit was read out nondestructively using a similar reading scheme. Half the read voltage (+2.5 V) was applied on the word line and half the voltage was applied on the bit line (−2.5 V). The read-out voltage therefore amounts to +5 volts. All other lines were grounded. The current was measured in time. As the measurement time elapsed, different word and bit lines were selected to probe the resistance of all 4 bits. The measured logic table is presented in Fig. 3. We distinguish three different current levels. When none of the bits are addressed the current level is dominated by noise and amounts to 10^{-10} A. The current level of a bit in the Off-state, state "0," is in the order of 10^{-9} A and corresponds to the off current of the diode in reverse bias and to the parasitic leakage current of the array. The On-state current, state "1," is in the order of 10^{-5} A, which corresponds to the space-charge limited current as measured for the discrete diode. The variation in the on-state current between the different bits is presumably due to thickness variation in the film. The logic table of Fig. 3 shows that the 16 different logic states of the 2×2, or 4-bit, array can easily be distinguished. The striking feature of the logic table is the identification of the 1110, 1101, 1011, and 0111 states. These states are most prone to cross talk but the high resistance "0" bit can still unambiguously be assigned.

To further demonstrate the feasibility of the ferroelectric diodes we also fabricated 9-bit memory arrays in a $4F^2$ cell configuration, where F is the width of the electrode lines and spacing between them, here about 3 mm. A picture of the array is presented in Fig. 4(a). The logic table comprises 512 different states. The equivalent circuit of the most challenging state, the state that is the most sensitive to cross talk, is presented in Fig. 4(b). A single high resistive bit "0" is in the center of the array and surrounded by eight low resistive "1" bits. Figure 4(c) shows the current passing through each individual bit as the measurement time elapsed. The most challenging state, 111101111, can be clearly read out.

Key device parameters for memory application are switching time, cycle endurance, and data retention of the individual pixels. The switching time of the array is dominated by the polarization reversal of the ferroelectric. The switching exponentially decreases with electric field. Although in our array the switching time is in the order of

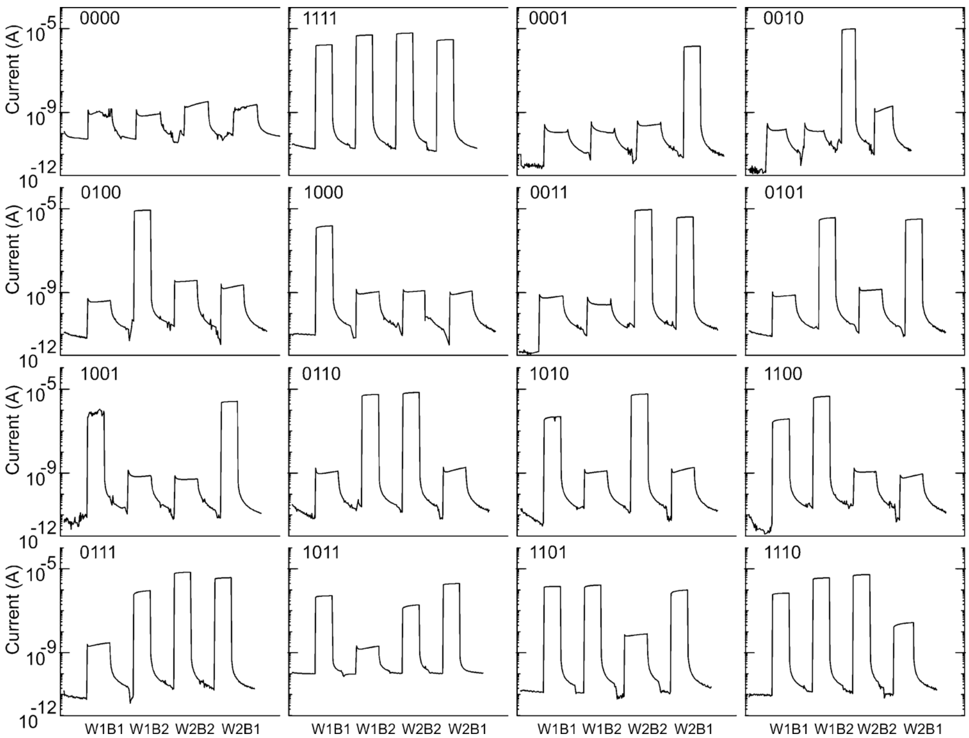

FIG. 3. Logic table of a 4-bit memory array given in Fig. 1(b), comprising 16 different logic states. The off-state current level, "0," is 10^{-9} A. The on-state current level, "1," is 10^{-5} A. The experimental noise level is about 10^{-10} A. The striking feature is the identification of the 1110, 1101, 1011, and 0111 states. These states are most prone to cross talk but the high resistance "0" bit can still unambiguously be assigned.

microseconds, shorter switching times have recently been reported.[13] Cycle endurance and data retention of the array are dominated by those of the individual bits. Discrete diodes already have shown cycling endurance of more than 1000 cycles and data retention for more than a week,[12,14] further optimization of reliability is beyond the scope of this manuscript.

In summary, we have demonstrated a functional cross bar memory array using an unpatterned storage medium; a phase separated blend of a ferroelectric and a semiconducting polymer. Each intersection acts simultaneously as a bistable rectifying diode. A logic table of a 2×2, 4 bit, array has been experimentally verified. Further feasibility of the ferroelectric diode based cross-bar memory has been demonstrated with a 3×3 or 9-bit array. The most difficult state, a high resistance bit completely surrounded by low resistance bits could be unambiguously identified. This demonstrates a step forward toward the "immortal memory," a cross-talk free memory array with an unpatterned storage medium.

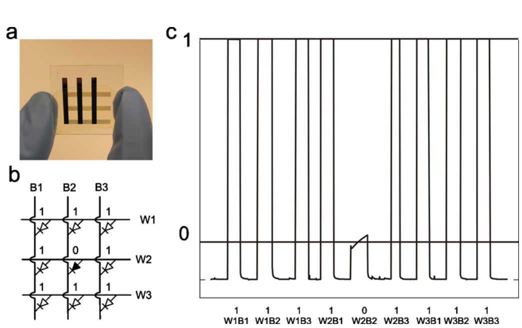

FIG. 4. (Color online) (a) A photograph of a 3×3 crossbar memory array. The electrode linewidth and spacing are about 3 mm. (b) Equivalent circuit of the 3×3 array shown in Fig. 4(a); programmed into the 111101111 logic state. (c) The current passing through each individual bit in the 111101111 logic state as the measurement time elapsed. The measurement shows that cross talk is eliminated; the programmed state is nondestructively read out.

The authors gratefully acknowledge technical assistance from J. Harkema at the University of Groningen, and MiPlaza, Eindhoven. The research leading to these results has received funding from the Zernike Institute for Advanced Materials, University of Groningen, The Netherlands, and the European Community's Seventh Framework Program (FP7/2007-2013) under grant Agreement No. 248092 of the MOMA Project.

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